Adsorption and Desorption Rates of Particulate Mercury and Dissolved Isotopically Enriched Mercury Determined By MC-SF-ICP-MS

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Setting standards in analytical science

Aim

To monitor the rate of adsorption of isotopically enriched Hg and the rate of desorption of natural isotopic abundance particulate Hg during isotope dilution analysis (IDA) equilibration.

Isotope Dilution Analysis Procedure

IDA consists in adding a known quantity of the target analyte, enriched in one isotope, to a sample so that the isotopic composition of the target analyte in the sample is modified.

By determining the modified isotope amount ratio between one isotope of the target analyte (^{200}Hg) and the isotope (^{199}Hg) enhanced during the spiking procedure the mass fraction of the element in the sample can be calculated.

Experimental

A known mass of particulate Hg (via NIST2710 Montana soil CRM) and an equivalent mass of ^{199}Hg enriched mercury was added to a known volume of the equilibration solution (50:50 methanol:water *v\v*, 0.01% 2-mercaptoethanol. 1ml aliquots of the equilibration mixture were withdrawn with time and filtered.

The ^{200}Hg:^{199}Hg isotope amount ratio and the mercury concentration in the withdrawn aliquot were subsequently determined by multicollector sector field (MC-SF) and quadrupole(Q) ICP-MS. Equilibration between the available natural particulate mercury and the ^{199}Hg enriched spike was adjudged to be complete when the measured isotopic amount ratio was constant with time.

Isotope Amount Ratio Measurement

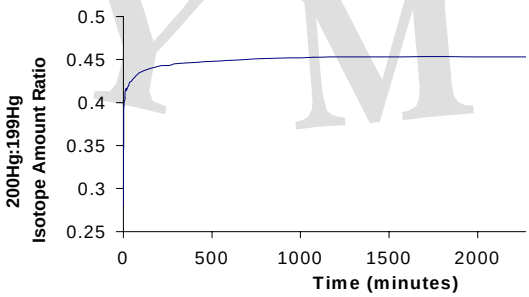

Figure 1: Rate of change of the ^{200}Hg:^{199}Hg isotope amount ratio with time.

The measured ^{200}Hg:^{199}Hg isotope amount ratio was corrected for mass bias with NIST997 Tl as an internal standard. The relative expanded uncertainty (k=2) for the corrected isotopic ratios was ≥ 0.06% for the MC-SF instrument and ≥ 0.7% for quadrupole determinations. The major contributions to the expanded uncertainty are shown in Table1.

Table 1: *^{200}Hg:^{199}Hg Isotope Amount Ratio Uncertainty Contributions*

Isotope Amount Ratio	Relative Uncertainty Contribution (%)	
	Axiom MC-SF-ICP-MS	PQ3 Q-ICP-MS
Measured ^{200}Hg:^{199}Hg	36	71
Measured ^{205}Tl:^{203}Tl	45	27
NIST997 CRM ^{205}Tl:^{203}Tl	19	1

Adsorption and Desorption of Hg

Initially the natural abundance mercury was rapidly desorbed from the particulate material before undergoing readsorption, with less than 15% desorbed at equilibrium. 75% of the enriched spike mercury was adsorbed to the particles. The expanded uncertainty (k=2) in the amount of mercury desorbed/adsorbed from or to the particles was dominated (99%) by the uncertainty contribution of the estimation of the concentration of mercury in solution.

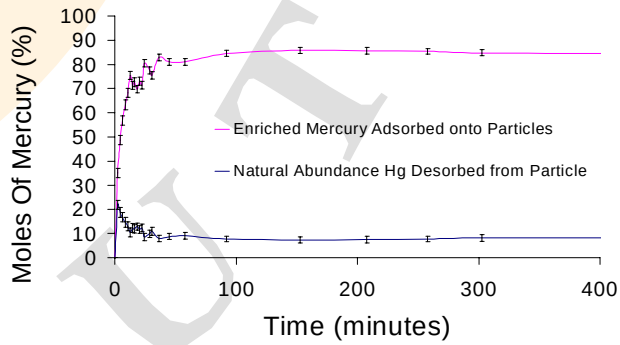

Figure 2: Desorption and Adsorption of particulate and aqueous mercury respectively. Error bars are the expanded uncertainty (k=2).

Mercury Concentration By Isotope Dilution Analysis

The proportion of methanol in the equilibration solvent was varied and the experiments repeated. The NIST2710 CRM mercury concentration, certified as 32.6 ± 1.6 µg/g, was calculated by isotope dilution analysis (IDA) using the measured ^{200}Hg:^{199}Hg isotope amount ratio at equilibrium.

Methanol (%)	*NIST2710 CRM* [Hg] *by IDA* (µg/g)	*Expanded Uncertainty* (µg/g) (*k=2*)
50	22.4	0.64
80	27.6	0.79
20	24.9	0.72

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